Photonic Sintering of Silver for Roll-to Roll-Printed Electronics

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Introduction

The use of high energy pulsed light is presented as a means of sintering printed nano-particle inks to form conductive traces on flexible substrates. These novel metal nanoparticle based inks are ideally suited for photonic sintering due to changes of their basic physical properties based on their size. A phenomenon referred to as melting point depression is related to the change in the surface to volume ratio of the particles allowing sintering to take place at temperatures significantly lower than that of the bulk material. Another relevant physical change is the interaction of nanoparticles with light. As these particles have sizes that are smaller than the wavelength of light, plasmon effects can occur which allows increased efficiency in photonic energy absorption as heat.

Conventional printed electronics fabrication is typically a subtractive process where chemical or enchants are used in conjunction with a photo lithographic process to define functional conductive traces. Printing conductive traces and photonic sintering is conversely a simple additive process where no additional chemicals are used or material wasted and therefore can be considered as clean technology.

Current common practice for sintering nanoparticles is to use a low temperature oven for tens of minutes set at a sufficient temperature to sinter yet not damage the substrate. However this kind of process does not lend itself to a roll-to-roll production process. The use of high energy pulsed light from a Xenon arc lamp is a novel approach that has the advantages of being fast, often effectively sintering in a matter of milliseconds, as well as being a low temperature solution harmless to the substrate. The pulse widths of these sources are in the order of microseconds with peak energies in the Mega-Watt region. By offering meaningful control of the pulse energies, pulse width and number of pulses required, this same technology can be applied to varied process requirements based on substrates, ink types, printing technology and process speeds.

There are a number of evolving nano-ink formulations that are available in the industry of which one of the more commonly used is silver. This experimental study of photonic sintering optimizes the process and deals with challenges of stitching, uniformity and effective resistivity changes. The object of this work is to define the parameters for a roll to roll deployable system for flexible circuit fabrication based on roll speed; number of flash lamps required and desired resistivity values. Two different substrates have been studied in these experiments, one being paper and the other PET and comparisons are drawn between them. This study proves the efficacy of Photonic Sintering of silver and establishes it as a viable, practical and cost effective solution for a roll-to-roll integrated process.

The most important challenge for photonic sintering is that of resistivity. Copper, silver and gold which are often used in PCBs are very good conductors and have very low resistivity. This property allows circuits to run more efficiently. Conduction though metals happen because electrons are free to move about the metal lattice. When metal clusters are deposited in ink form, resistance is increased because the lattice is disjointed. Gaps and voids between metal particles do not allow the free movement of electrons and this causes an increase in the resistance. Ideally, the metal particles need to be melted together or sintered to form a homogenous strip of metal to achieve better resistivity. However melting points of metals are typically very high. Gold as an example melts at 1064 °C and this amount of heat means that low temperature substrates such paper and PET as are not useable. All this

has changed with the advent of Nanoparticles based inks.

Nanoparticles are defined as particles that have a size between 1nm and 1000nm. More generally speaking, however, particles with sizes up to 100nm are referred to as nanoparticles. As particles become smaller their physical characteristics are changed. These physical characteristics include their absorption characteristics and melting point. Melting point depression is a phenomenon expressed by metal nanoparticles. In normal scales the melting point of the material is not dependent on size. As particles become smaller, their surface area to volume ratio changes causing the atoms on the outer surface become more loosely attached and this causes a lowering of the melting point. As the melting point is depressed, the use of low bake oven which maintains a temperature below 200C makes it possible for sintering of nano-inks without damage to the substrate. The time required for this process is around 10s of minutes and therefore makes application to roll to roll processing difficult.

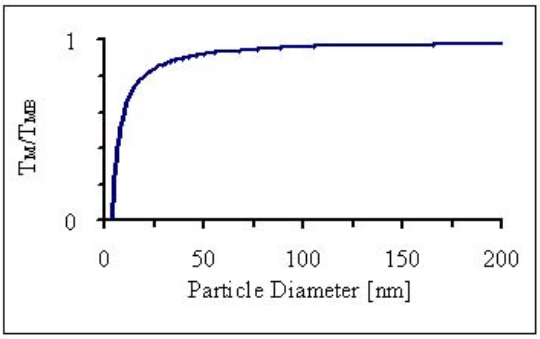

Figure 1. Graph showing how particles size affects the melting point of gold. After the particles become more than 100nm. Their melting point is very close to that of bulk material.

Another feature of nanoparticles is the way that they react with light due to the fact that the particles themselves are smaller than the wavelength of light. This absorption characteristic change can allow particles to absorb light and heat up.

Melting point depression and absorption changes allow nanoparticles to be sintered effectively with high energy light sources such as lasers or flash lamps. Using flash lamps is significantly simpler when compared to lasers, particularly when large area processing is required. Also the use of a broad band source such as those generated with a Xenon Flash lamp is more effective particularly as typical inks have a spread of particle size and a wide absorption region.

Once nanoparticles are sintered, they loose their nanoparticle properties and behave similar to bulk material. The process therefore is self limiting in that multiple flashing does not significantly improve the resistivity and limited sintering takes place. This behavior raises an important challenge in the use of pulsed light for sintering related to stitching. All light sources have a limited exposure area. The boundary between the exposed area and unexposed area creates partial sintered regions. When two adjacent boundaries are flashed, the overlap region is defined as the stitch. These partial sintered regions when flashed again behave differently to those areas that have been exposed fully once and this can be observed as differences in the resistivity across the stitch region. Careful control of the boundary profile, light energy and overlap can reduce the effect of stitching significantly. However the most significant factor is the nano-ink formulation that is used. Some inks do lend themselves to multiple flashing and in these inks the effect of stitching can be generally mitigated.

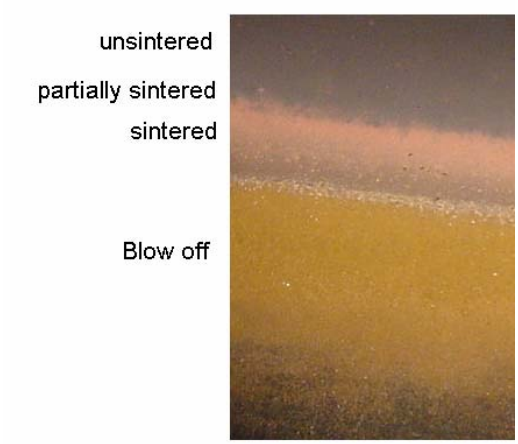

Figure 2. Image showing copper Nanoparticle based ink on Teflon that has undergone photonic sintering. With too little energy no sintering action happens when there is too much energy particles are removed and only the substrate remains.

Resistivity of sintered inks is generally higher than that of bulk material and this is

because of the remaining porosity of the final material after sintering. Typically, resistivity values of 4 to 5 times that of bulk is considered a good result. Some self drying inks can achieve resistances of 6 times of the bulk. Photonic sintering to date has achieved results ranging between 3 and 5 times the bulk for certain inks.

Ink formulation plays a major role in the photonic sintering process. The method of depositing the ink must be suited to the ink in terms of viscosity and surface tension. The formulation also determines the drying time for the inks and the adhesion of the ink to the substrate. It has been observed that photonic sintering performs better with dry ink as opposed to wet inks. This is because pockets of solvent that are trapped in the ink are likely to expand and erupt when exposed to a high energy light pulse. This causes blow off of inks from the surface leading to a reduction in resistivity.

Another important factor to consider is the substrate that is used. Interestingly, paper is a very good substrates as they can absorb the ink and wick away the carrier agents in the ink. This allows the ink to dry better and also improves adhesion between the substrate and ink. PET and Teflon are also good substrates to use as they are good insulators and so allow more photonic energy to be absorbed by the ink rather than the substrate. Often these substrates are transparent and this means that they absorb less light and so allow for higher energy pulsed light for the sintering process.

Xenon Flash Lamps

Flash lamps have the ability to generate light with wideband spectra which range from the deep UV to the infrared. By using high energy flash lamps high peak power pulses can be generated. They are capable of delivering significantly greater peak energies compared to continuous sources like mercury, fluorescent or halogen lamps, by storing energy over time and delivering it as a short duration high intensity pulse. This high peak pulse energy is sufficient to cause sintering to take place. Xenon arc lamps generate light by using high voltage to breakdown the inert gas within the lamp envelope creating a conductive discharge path where the flash exists. Because typical flash lamp use is with a very short on time compared with off time, they are very effective at delivering high peak photonic power without significantly increasing the surface temperature of the object being illuminated and substrate temperature rise can be very small in the range of a few degrees.

For roll-to-roll systems, simplicity is the key to successful deployment of the process. From this perspective the solution offered by photonic sintering looks very attractive. First we have an ink deposition phase which lends itself to standard printing processes. Then an ink drying phase takes place which is also standard. The only additional step is the photonic sintering phase which can be as easy as a retro fit of a Xenon flash lamp system over the web. There are no additional process requirements like pressure, special gas or chemicals. Dwell time in the photonics sintering is not an issue as the reaction is instantaneous as opposed to thermal sintering which can take minutes. What does need to be considered, however, is the pulse rate, to control the overlap of the photo-sintered regions avoiding overexposure or banding if there is a gap between the two adjacent regions. To be a versatile solution, scalability becomes an important factor specially when considering different roll to roll speeds and ink formulations. Photonic sintering systems can be easily scaled by increasing the number of lamps required for a given process speed.

The flexibility of the technology can be illustrated by considering the range of different materials and substrates that have been successfully processed with low temperature photonic sintering at Xenon. These include, Silver flakes, Silver Nano inks, ITO, Copper inks and Gold.

A Case Study on Silver Sintering;

Tests were performed on silver flake based inks on paper and PET which was printed at Western Michigan University. The advantages of these flakes are

a) Once dried these inks have some conductivity prior to sintering.

b) Multiple pulses of Light can incrementally improve resistance
c) The process window of acceptable optical energy required for sintering is quite large.

These inks were Gravure printed onto paper and PET Substrates and air dried. Static testing was performed using a 16 in linear flash lamp source operating at 10Hz and 207 J per pulse. After one second exposure the resistance was reduced by 80%. This reduction in resistance was comparable to those achieved after 10 minutes treatment in a low bake oven. No damage to substrate was seen for both paper and PET. The treatment seemed asymptotic suggesting that maximum gains are achieved with only 4 pulses after which the resistance dropped by 40%. Initial static testing yielded that PET was marginally better than paper as a substrate. Tests were performed on a conveyor system with a single lamp system. The flash rate and conveyor speed was adjusted to get 80% overlap between consecutive pulses. No visible stitch marks were observed. Resistivity measurements across stitch boundaries showed only a marginally lower resistance compared with a normally sintered region.

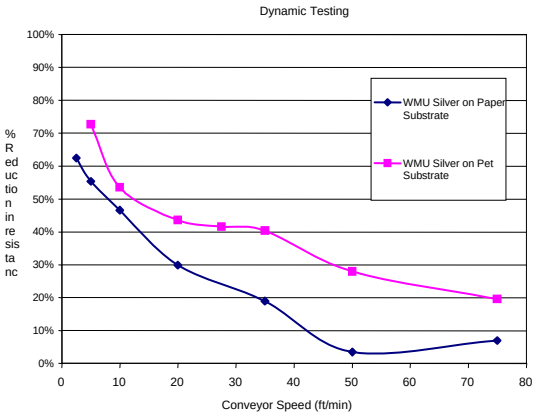

Figure 3. Graph showing results of dynamic testing of photonic sintering of silver ink on PET and Paper in terms of resistivity and Conveyor Speed

Based on these experimental results a table was generated that could help in defining the system requirements in terms of number of lamps required based on the roll to roll speed and the net Resistivity reduction required.

Based on this table a three lamp system was evaluated with the conveyor operating at 30 ft/min which could attain a 50% reduction in resistivity.

Desired Reduction %

	5	10	15	20	25	30	35	40	45	50	55	60	65	70
2.5	1	1	1	1	1	1	1	1	1	1	1	1	1	1
5	1	1	1	1	1	1	1	1	1	1	1	1	1	1
10	1	1	1	1	1	1	1	1	1	1	2	2	2	2
15	1	1	1	1	1	1	1	1	1	2	2	3	3	3
20	1	1	1	1	1	1	1	1	2	2	3	3	3	4
25	1	1	1	1	1	1	1	1	2	3	4	4	4	5
30	1	1	1	1	1	1	1	1	2	3	4	5	5	5
35	1	1	1	1	1	1	1	1	3	3	5	5	5	6
40	1	1	1	1	1	1	1	2	3	4	5	6	6	7
45	1	1	1	1	1	1	2	2	3	4	6	7	7	8
50	1	1	1	1	1	2	2	2	3	5	7	8	8	9
55	1	1	1	1	1	2	2	2	4	5	7	8	8	10
60	1	1	1	1	2	2	2	2	4	5	8	9	9	10
65	1	1	1	1	2	2	2	2	4	6	9	10	10	11
70	1	1	1	1	2	2	2	2	5	6	9	10	10	12
75	1	1	1	1	2	2	2	3	5	7	10	11	11	13
80	1	1	1	2	2	2	2	3	5	7	10	12	12	14
85	1	1	1	2	2	2	3	3	5	8	11	13	13	15
90	1	1	2	2	2	2	3	3	6	8	12	13	13	15
95	1	1	2	2	2	3	3	3	6	8	12	14	14	16
100	1	2	2	2	2	3	3	3	6	9	13	15	15	17

Figure 4. Required no of lamps for different speed and reduction goal

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The key to successful deployment of photonic sintering in the production arena will be in the development of flexible tools that can help the process developers, the ink formulators, the printing manufacturers and end users. These groups can then evaluate the technology and find solutions for their specific needs. To this end Xenon Corp has developed low cost R&D tools that allow groups to try out the technology. The Sinteron 2000 and Sinteron 500 are good examples of such systems offering flexibility in defining the energy delivered to the samples as static tests. For addressing issues related to larger areas, a linear stage can be integrated with the Sinteron family of products offered. Qualification of photonic sintering solutions provides essential input in the current development plan for production deployable roll to roll systems. It is clear that Photonic sintering will play a major roll in the future production of flexible electronics and will have far reaching consequences not only in this field but also in our every day lives in the future.

Figure 5. The Sinteron family of products for evaluation of Photonic Sintering